Emission Sources and Formation of Particulate Organic Matter (POM)

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A summary of observations from 1 airborne and 2 ship-based measurement campaigns in New England

Sources of Particulate Organic Matter (POM)

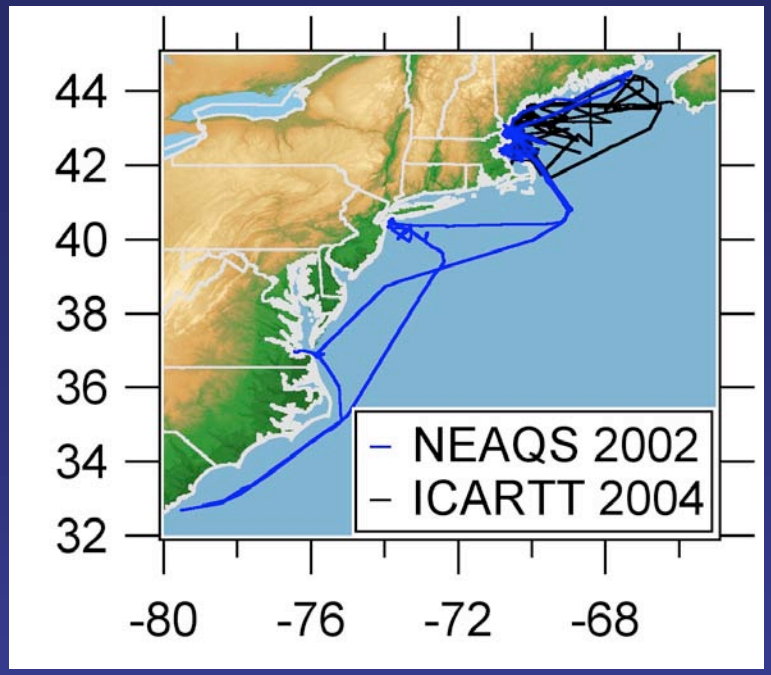
Direct Emissions			
Biomass burning			43.7 Tg y^{-1} [a]
Fossil Fuel combustion			3.2 Tg y^{-1} [a]
Secondary Formation			
Monoterpenes	130 Tg y^{-1} [b]	14% yield [c]	18 Tg y^{-1}
Isoprene	500 Tg y^{-1} [b]	0.9-3.0% [d]	4-13 Tg y^{-1}
Toluene	6.7 Tg y^{-1} [a]	11% [c]	0.7 Tg y^{-1}

[a] Kanakidou 2005, [b] Guenther 1995, [c] Seinfeld & Pandis 1998, [d] Kroll 2005

Bottom line:
- Direct emissions > secondary formation
- Most POM contains modern carbon

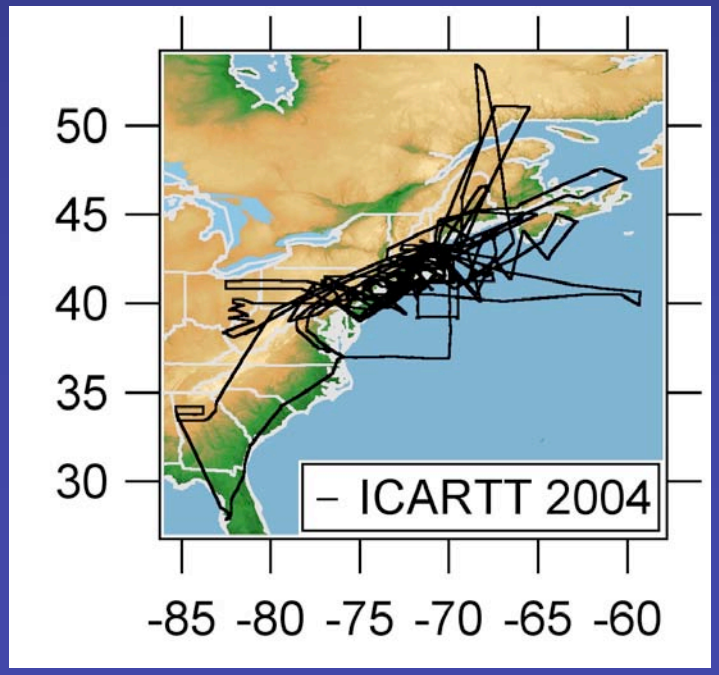
Our Observations in New England

1. POM was associated with urban emissions
2. POM was mostly secondary
3. Formation could not be explained from known precursors



2002: AMS Middlebrook
EC/OC Bates

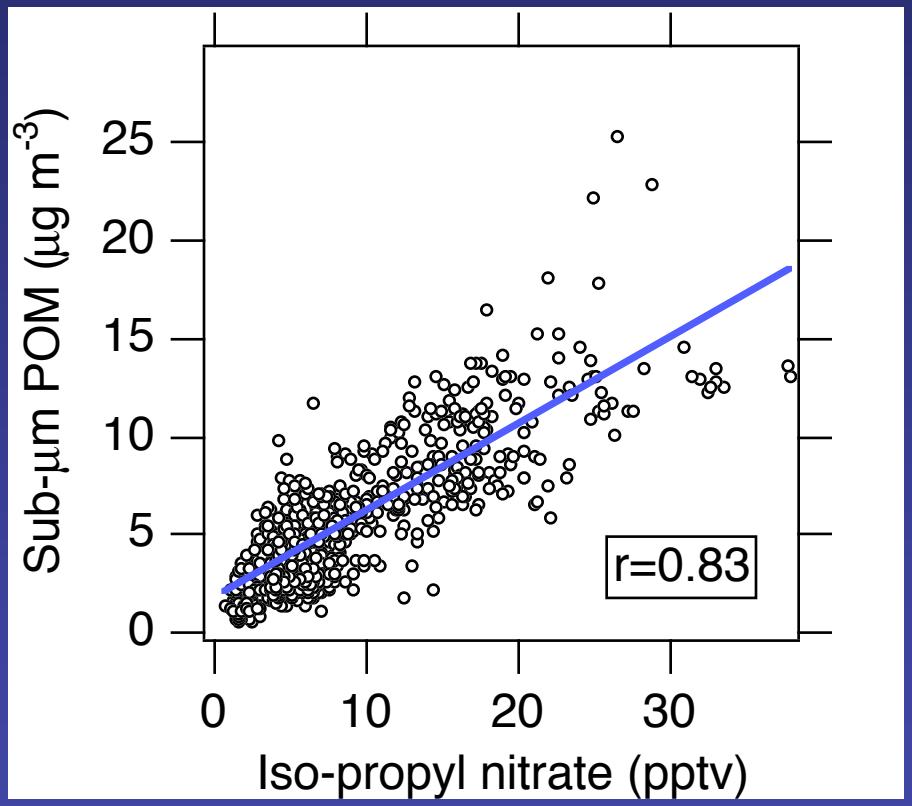
2004: AMS, EC/OC, WSOC
Quinn & Bates



2004: AMS Middlebrook
WSOC Weber

1. Mass loading of POM correlates well with urban pollutants

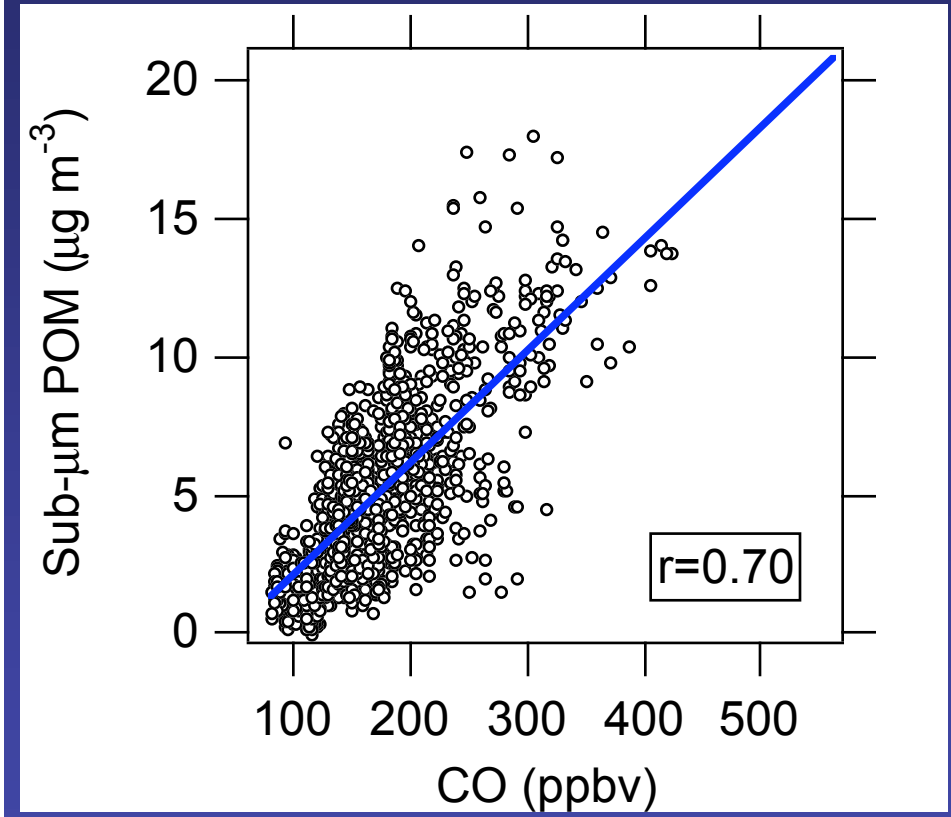
POM vs. Iso-Propyl Nitrate During NEAQS 2002



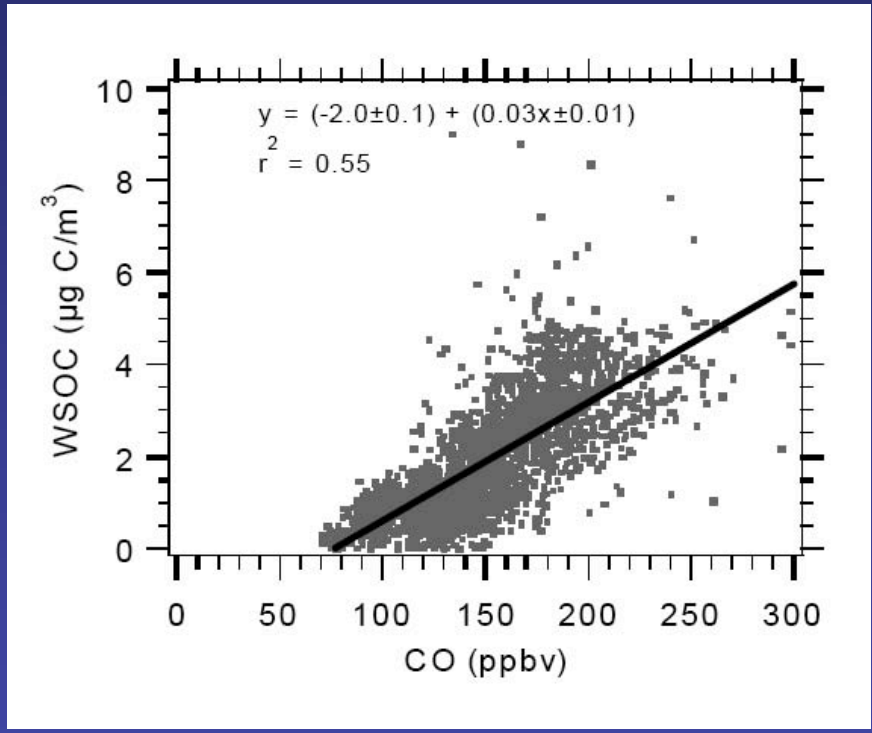
Iso-propyl nitrate is oxidation product from propane and other mainly anthropogenic hydrocarbons

(de Gouw, JGR 2005)

POM / WSOC vs. CO During ICARTT 2004

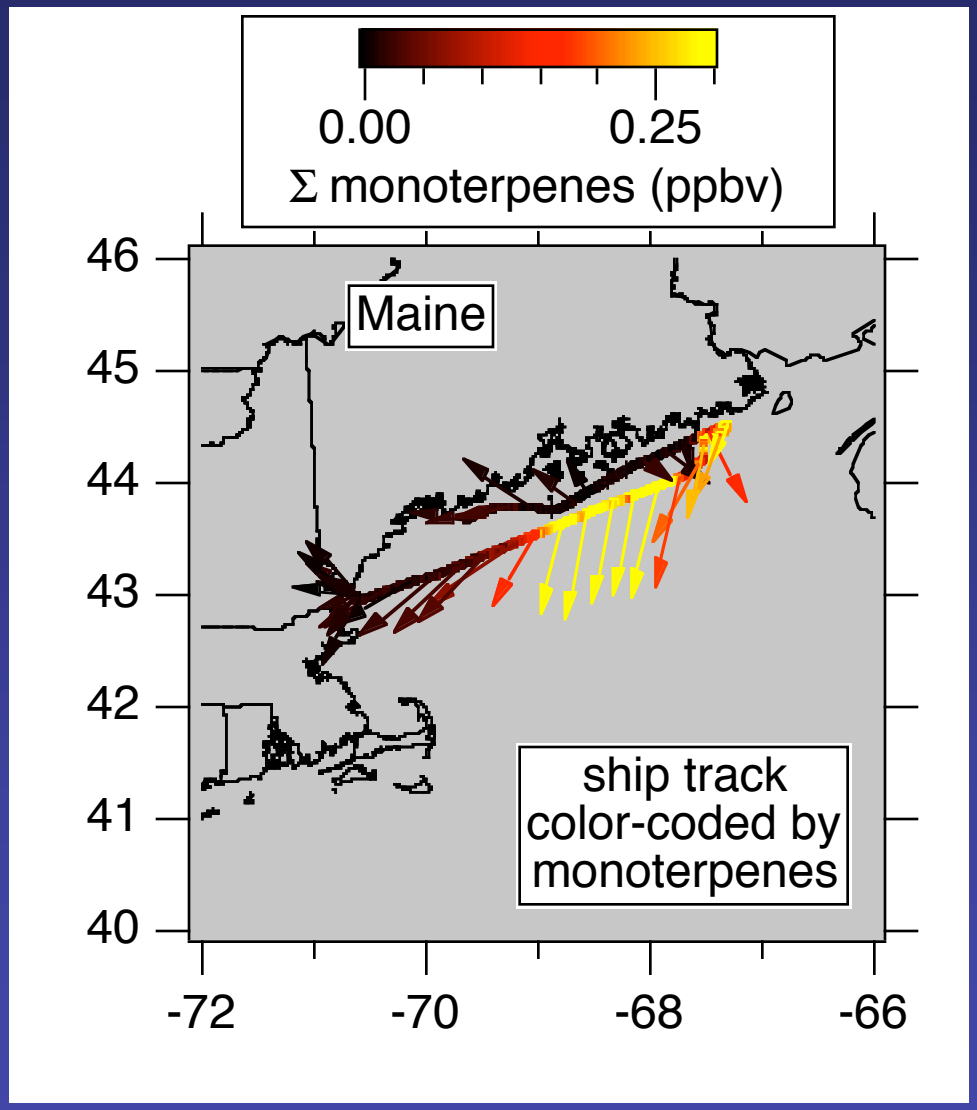


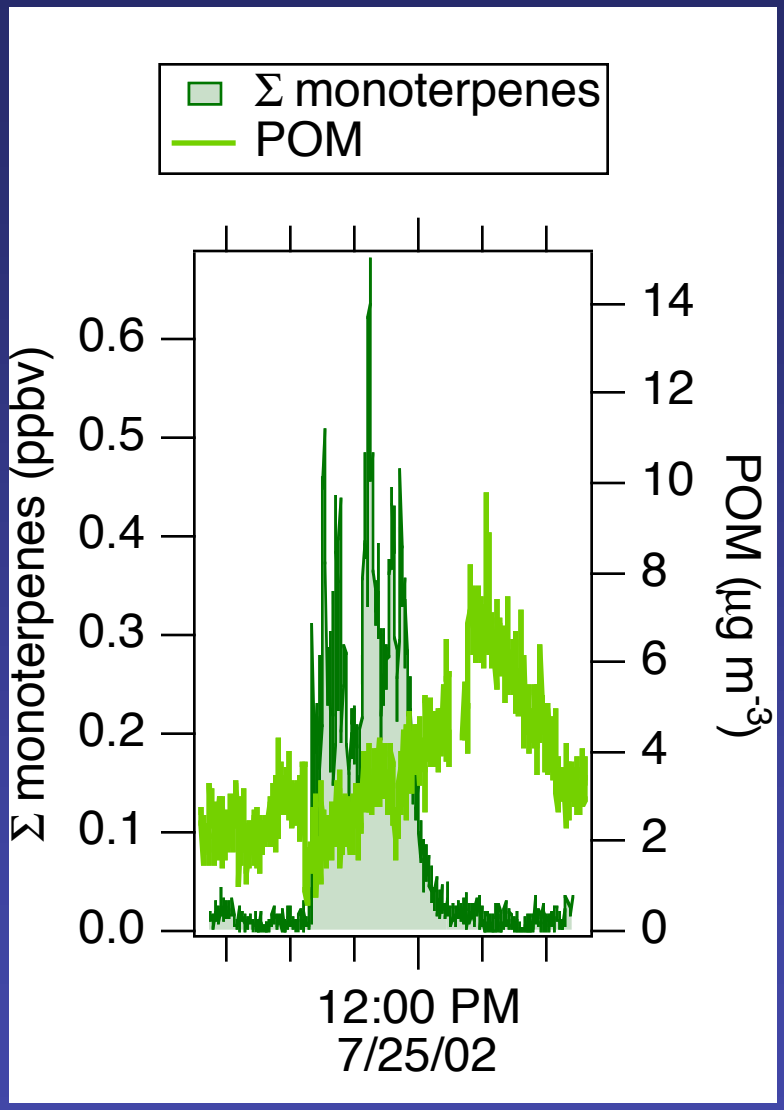
Ron Brown AMS data
(Quinn and Bates)



WP-3D WSOC data
excluding forest fire plumes
(Sullivan, JGR in press)

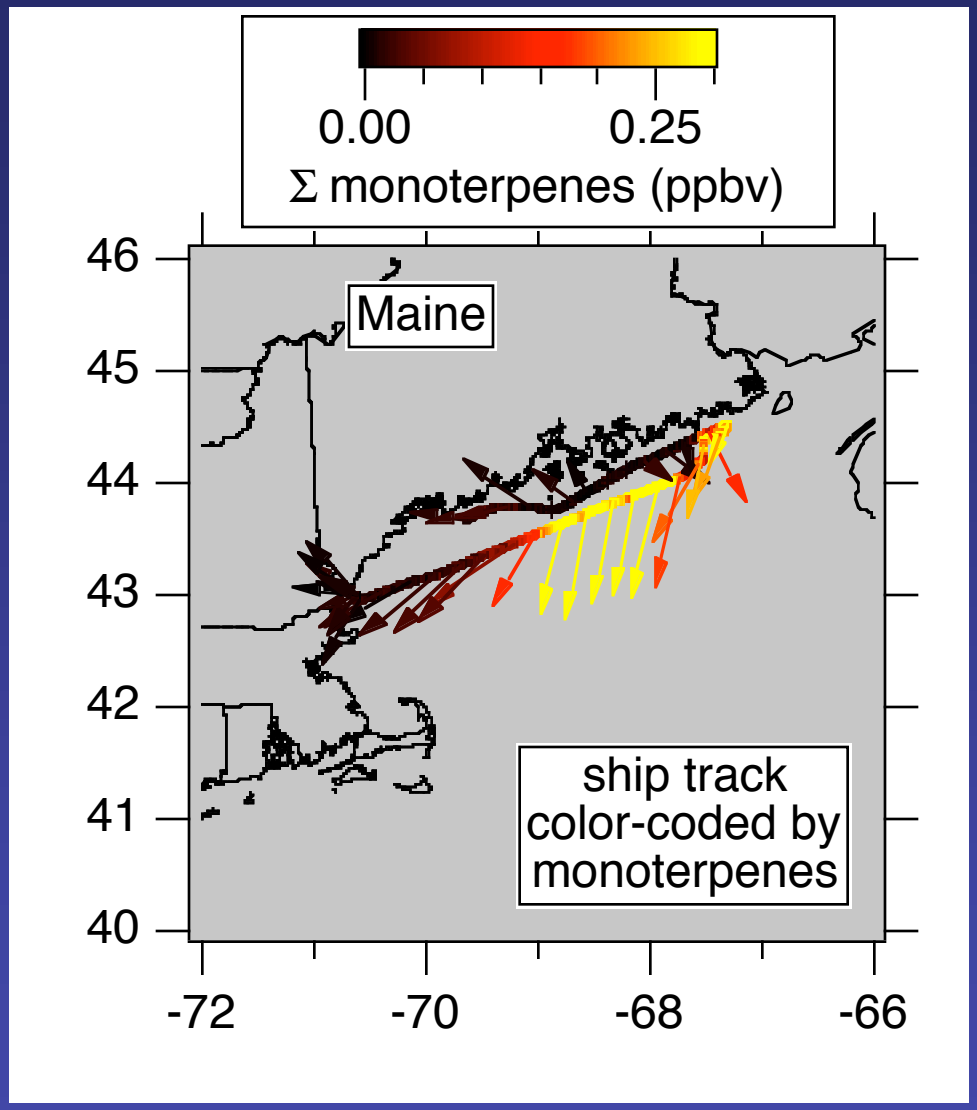
No Obvious Correlation with Biogenic Emissions

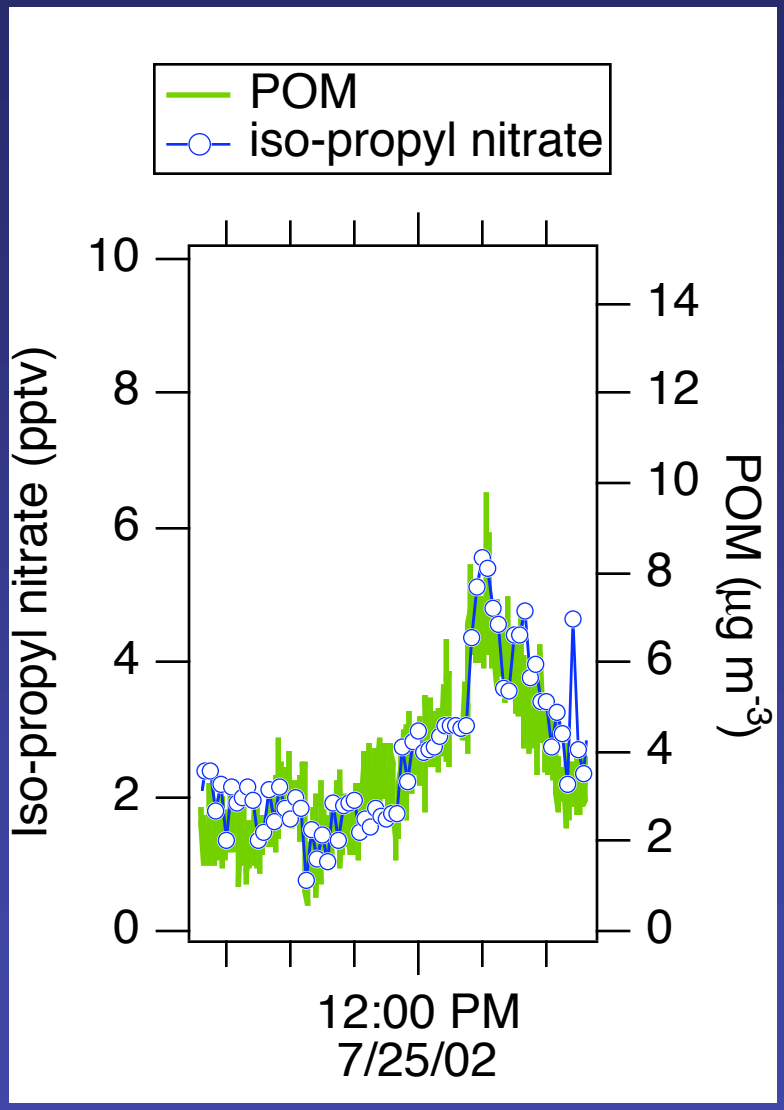




Ron Brown AMS data from NEAQS 2002

No Obvious Correlation with Biogenic Emissions

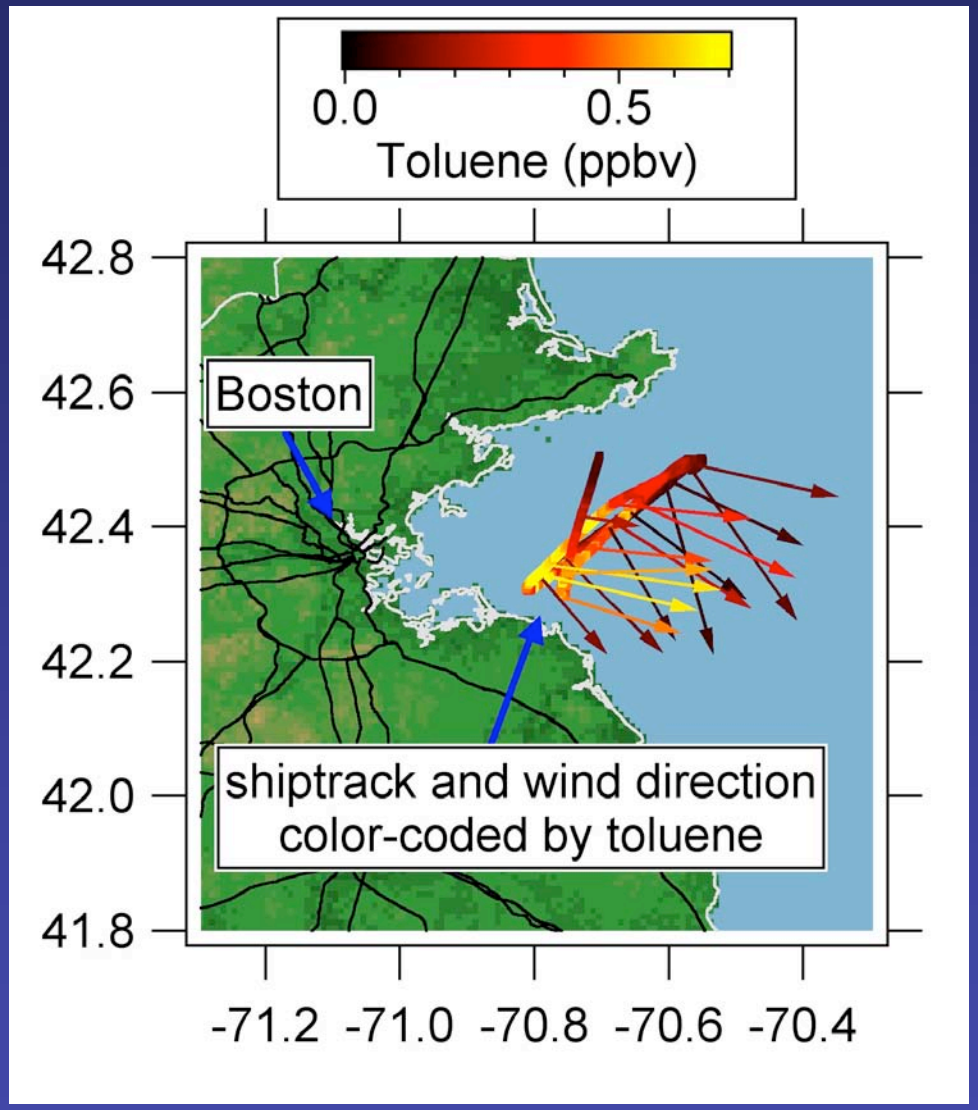


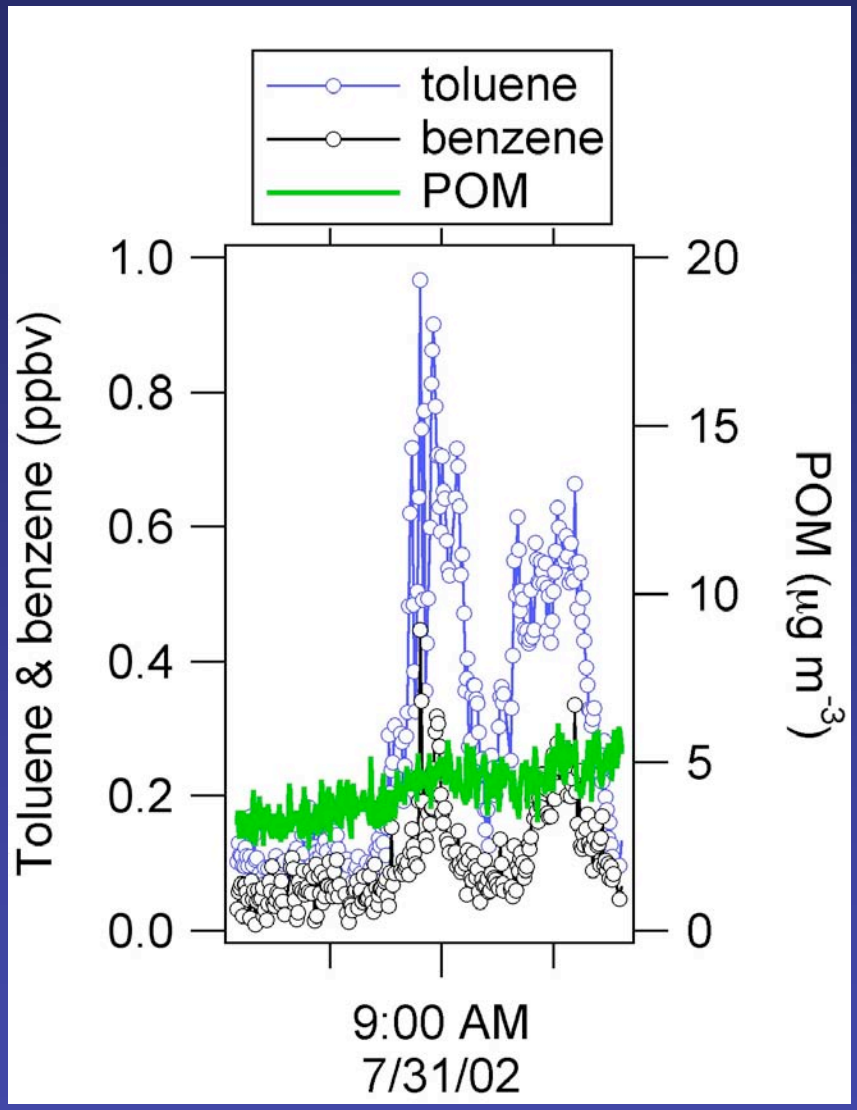


POM correlates better with fossil-fuel related emissions
⇔inconsistent with C14 data that says carbon is modern?

2. Direct, urban emission sources of POM are relatively small on regional scales

Direct, Urban Emissions of POM





- AMS data from NEAQS 2002
- Minor POM enhancements close to urban sources

Direct, Urban Emissions of POM

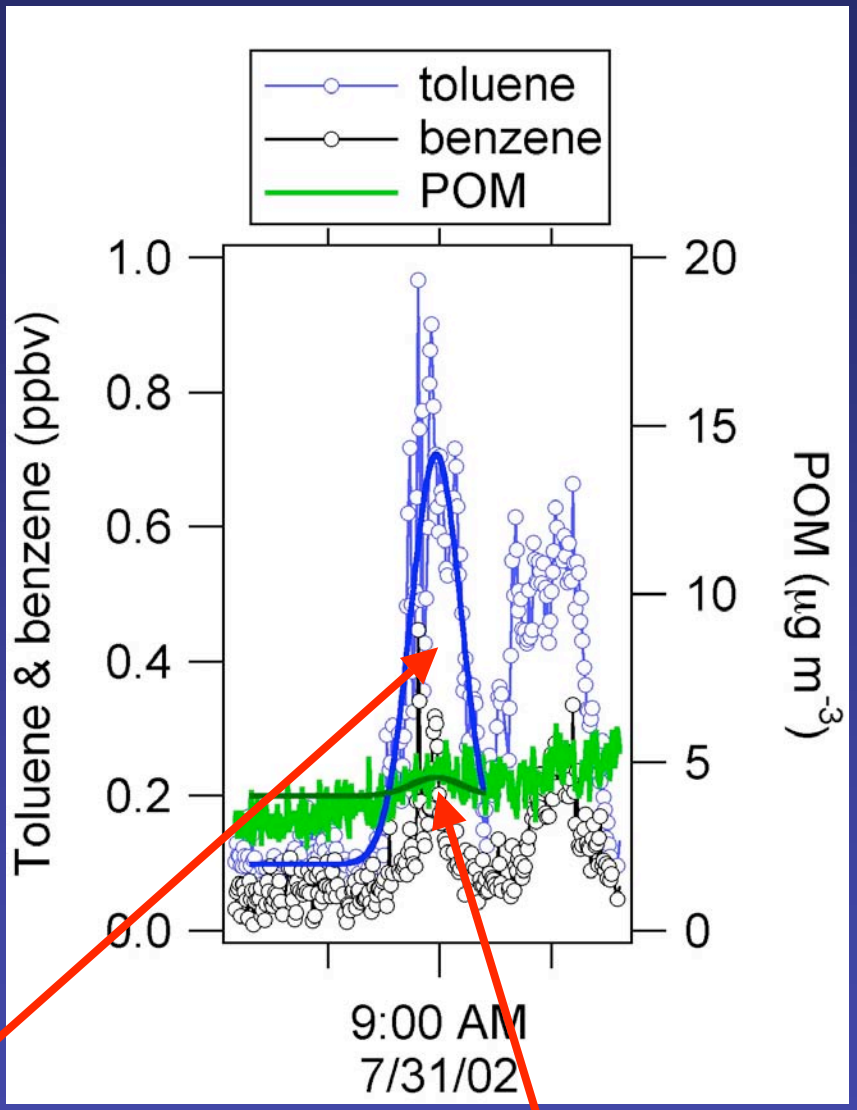
POM emissions from vehicles

$\Delta POC/\Delta CO = 2.1\ \mu g\ m^{-3}\ ppmv^{-1}$
(Kirchstetter, AE 1999)

$\Delta toluene/\Delta CO = 4.2\ ppbv\ ppmv^{-1}$
(Warneke, JGR in press)

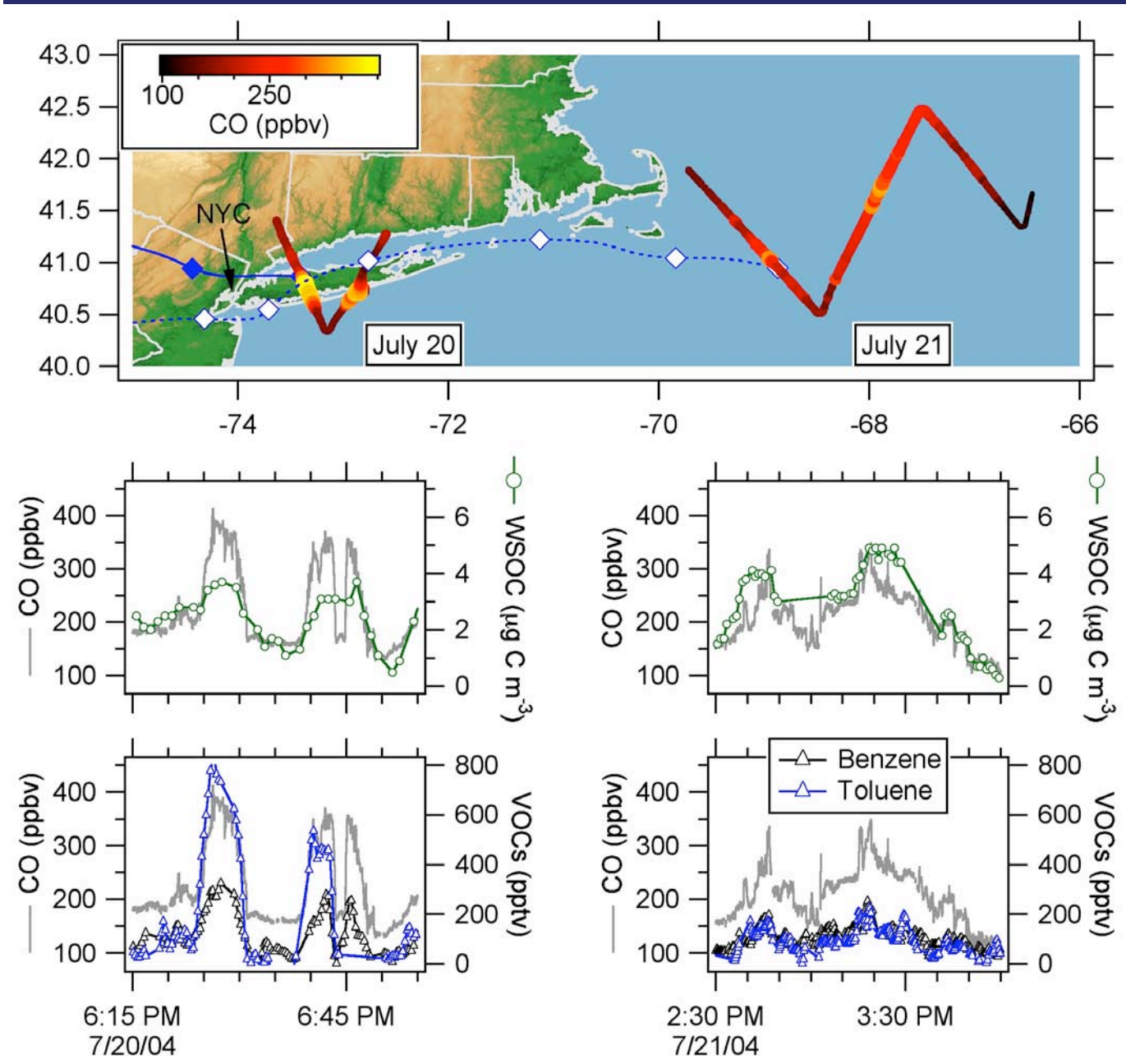
$\Delta POM/\Delta POC = 1.78$
(de Gouw, JGR 2005)

From which follows:
$\Delta POM/\Delta toluene = 0.9\ \mu g\ m^{-3}\ ppbv^{-1}$



$\Delta toluene = 0.6\ ppbv \Rightarrow \Delta POM = 0.5\ \mu g\ m^{-3}$

3. Mass loading of POM in urban plumes increases strongly in first 24 hours



WSOC Growth in NYC plume

WP-3D data from ICARTT

<u>ΔWSOC/ΔCO:</u>

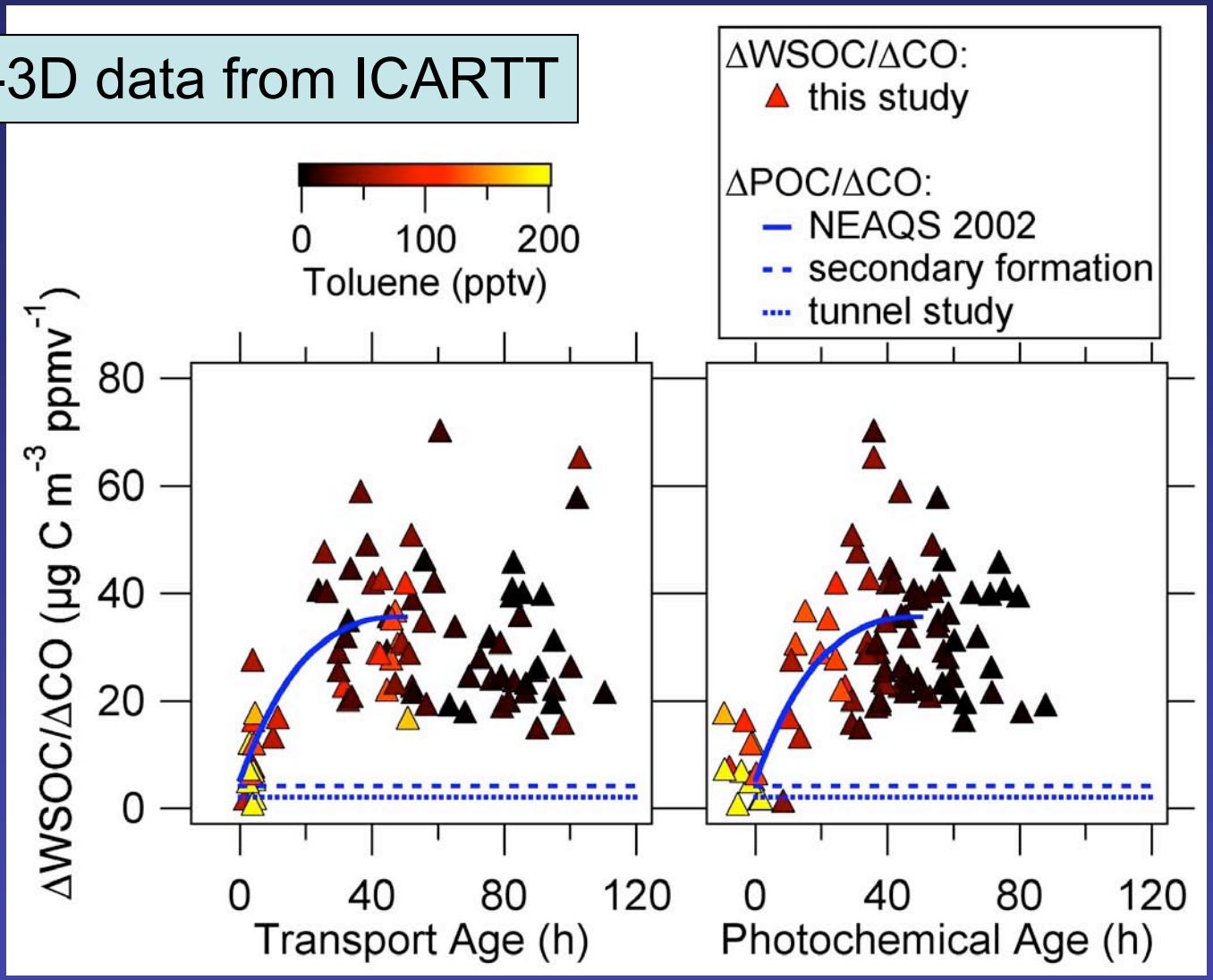
8.9 µg m^{-3} $ppmv^{-1}$ (July 20)

23 µg m^{-3} $ppmv^{-1}$ (July 21)

N.B. ΔOC/ΔCO: 2.1 µg m^{-3} $ppmv^{-1}$ (tunnel study)

WSOC Growth in Urban Plumes

WP-3D data from ICARTT

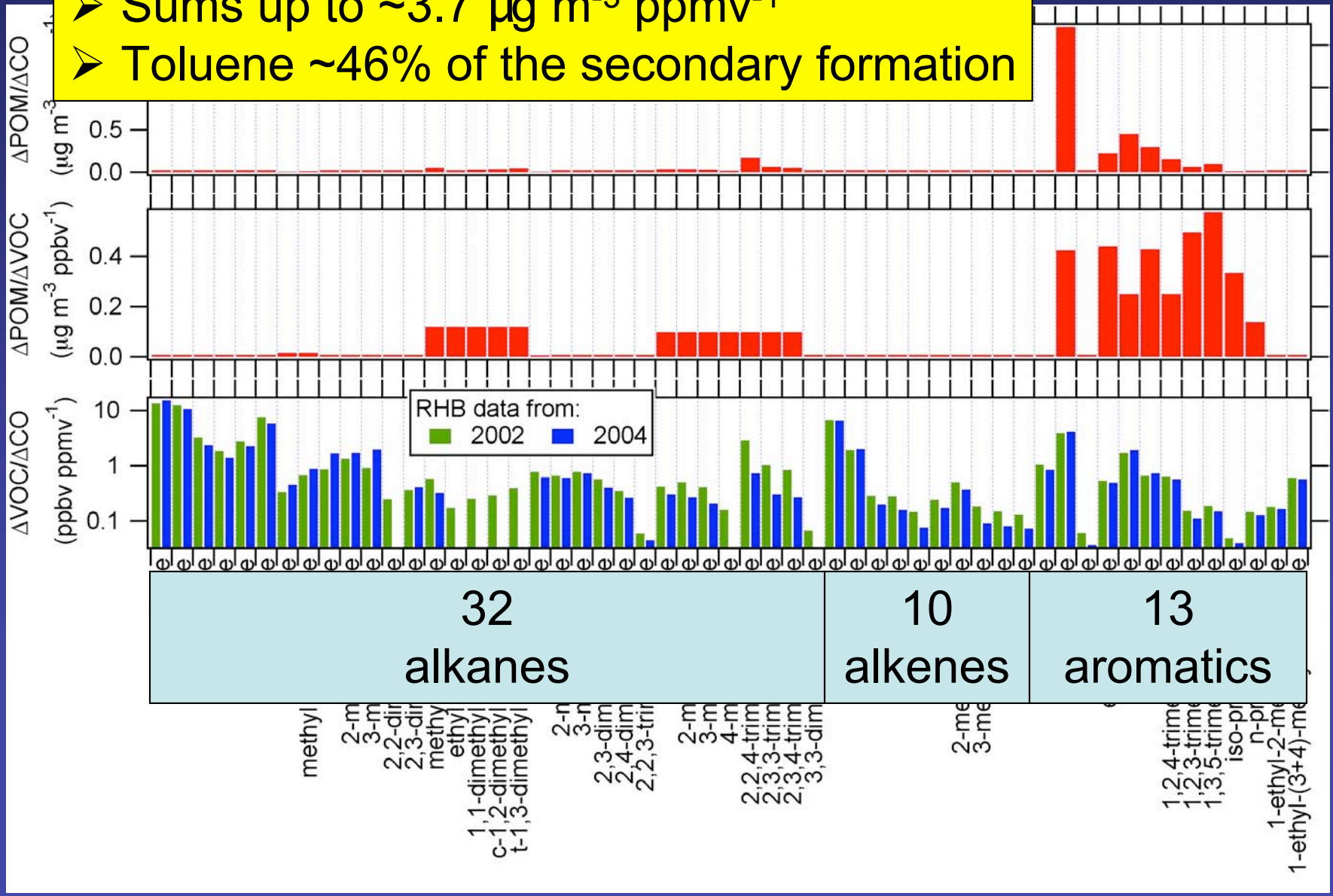


- Transport age from Flexpart or trajectories
- Photochemical age from benzene/toluene ratios

4. Increase in POM cannot be explained by removal of commonly measured VOCs

Secondary Formation from Measured VOCs

- Sums up to ~3.7 µg m^{-3} $ppmv^{-1}$
- Toluene ~46% of the secondary formation



WSOC Growth in Urban Plumes

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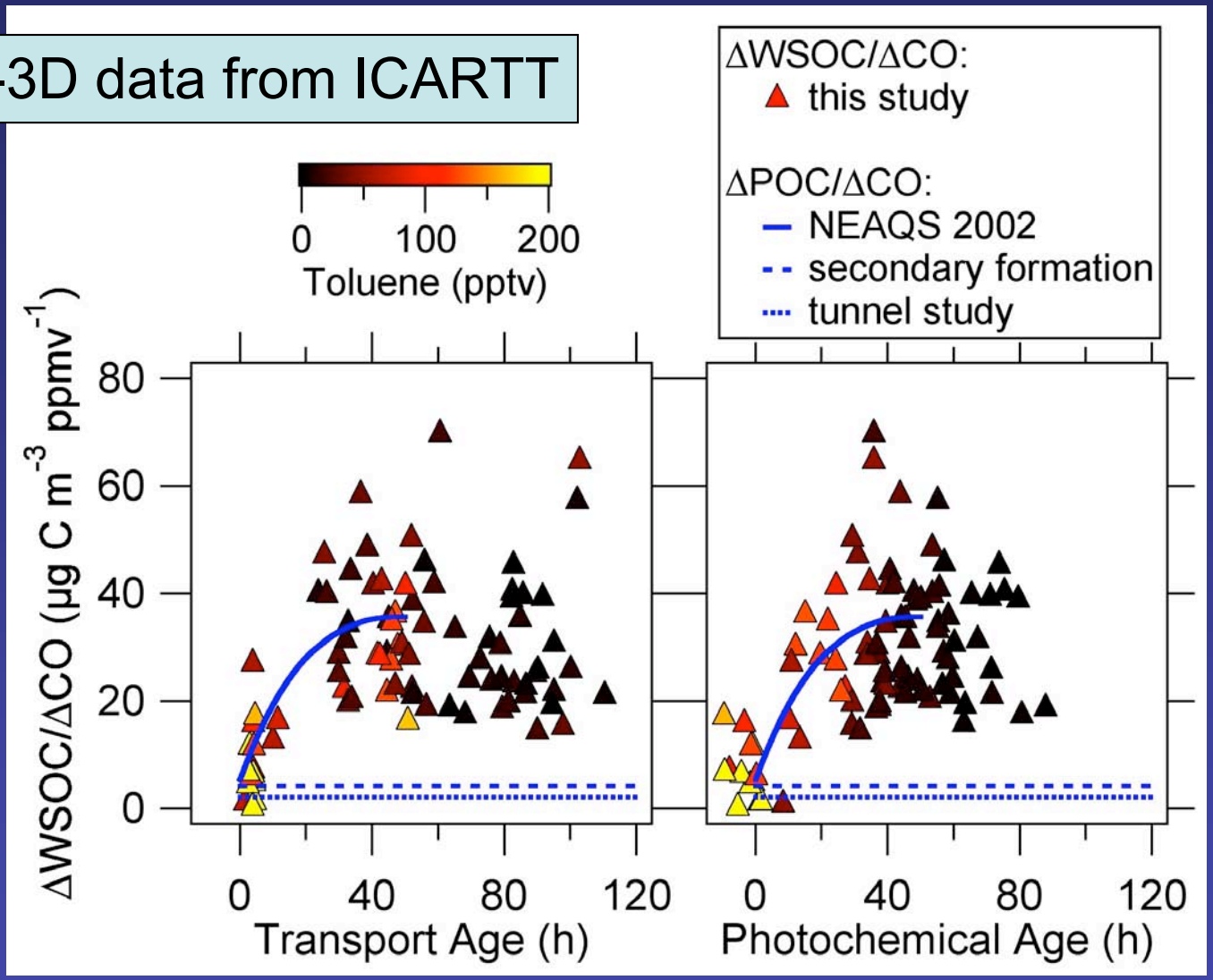

- Secondary formation from measured VOCs cannot explain the observed increase in POM

What Does it Mean?

Possible Explanations for the Discrepancy?

1. Formation from higher-mass VOCs?
   Donahue, ES&T 2006
   Only few measurements. Enough mass available?

2. Formation more efficient than observed in smog chambers?
   20% yield for all VOCs explains data

3. Formation from biogenic VOCs more efficient in urban air?
   Would explain correlation with pollutants
   Would explain the C14 data
   Biogenic precursors ≠ naturally occurring POM

Similar observations:

Heald, GRL 2005	*ACE-Asia*
Takegawa, GRL 2006	*Tokyo*
Volkamer, GRL 2006	*Mexico City*

Sources of POM: A Revision

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Biomass burning			43.7 Tg y^{-1}
Fossil Fuel combustion			3.2 Tg y^{-1}
Secondary Formation			
Monoterpenes	130 Tg y^{-1}	14% yield	18 Tg y^{-1}
Isoprene	500 Tg y^{-1}	0.9-3.0%	4-13 Tg y^{-1}
Urban Emissions			21 Tg y^{-1} [a]

[a] Assuming: 1. A global CO source of 450 Tg y^{-1}
2. Secondary formation of 30 µg C m^{-3} (ppmv CO)$^{-1}$

Bottom line: Secondary formation from urban emissions may be much higher than previously recognized

Acknowledgements

Ann Middlebrook	AMS
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